

Synthesis and Characterization of Copper(II) Sulphate Complexes With 2-, 3- and 4- Cyano-Pyridines and Anilines

I. S. AHUJA* and SHAILENDRA TRIPATHI

Chemistry Department, Banaras Hindu University, Varanasi—221 005, India

C. L. YADAVA

Chemistry Department, Kamla Nehru Institute of Physical and Social Sciences, Sultanpur—228 118, India

Coordination compounds of copper(II) sulphate with 2-, 3- and 4-cyano-pyridines and anilines have been synthesized and characterized on the basis of analytical data, molecular conductance, magnetic susceptibilities, electronic and infrared spectral measurements. Tentative coordination numbers and stereochemical environments around copper(II) are discussed in each case.

INTRODUCTION

Coordination compounds formed by copper(II) sulphate with aniline and its derivatives have been the subject of earlier investigations¹⁻⁵. The present communication describes the coordination compounds formed by the interaction of copper(II) sulphate with 2-, 3- and 4- cyano- pyridines and anilines. The importance of cyanopyridines and cyanoanilines lies in their relevant role in various biological processes⁶⁻¹¹ and their use in the synthesis of commercial dyes and thermally stable polymers¹². Various model studies have shown that metal complexes of biologically active ligands are more effective than the free ligands.

EXPERIMENTAL

2-, 3- and 4- cyanopyridines and anilines were purchased from M/s Ega Chemie, West Germany, and used as such. The copper(II) sulphate complexes were prepared by mixing together hot solutions of the copper(II) sulphate (10 mmol in 20 ml methanol) and the respective ligand (40 mmol in 10 ml methanol). The complexes which crystallized out or precipitated immediately were suction-filtered, washed with methanol and dried in an air oven at *ca* 60°C. (Yield *ca* 80-85% but in case of 2- cyano- derivatives yield is 10%). Copper content was determined gravimetrically as oxinate after destroying the organic moiety first with concentrated nitric acid and then with concentrated sulphuric acid. Sulphate was estimated as BaSO₄ gravimetrically. Carbon, hydrogen and nitrogen contents in the complexes were determined by microanalysis.

RESULTS AND DISCUSSION

The copper(II) compounds isolated in the present study, their analytical data, molar conductance data, room temperature magnetic moment

values, observed bands in the electronic spectra and the characteristic infrared absorption bands due to νCN , νNH and the sulphato modes are listed in Tables 1 and 2. All the compounds isolated are quite stable and are insoluble or partially soluble in ethanol and methanol. Except for the 2-cyanopyridine complex, they are fairly soluble in dimethylformamide in which solvent they behave as non-electrolytes¹³ ($\Delta_M = 1-3 \Omega^{-1} \text{cm}^2 \text{mole}^{-1}$) suggesting appreciable covalent character of the compounds. Insolubility of these compounds in molten camphor and biphenyl precluded their molecular weight determinations. Comparison of the infrared spectra of the copper(II) sulphate complexes with those of the corresponding uncoordinated ligand spectrum facilitated the assignment of bands due to sulphato groups. Strong bands due to sulphato groups in the range 1300-1000 ml^{-1} superimposed and masked some of the bands due to organic moiety. No absorption bands were observed which could be attributed to water or ethanol in the infrared spectra of these compounds thus establishing them to be anhydrous and free from coordinated or lattice water/ethanol.

Cyanopyridines and anilines possess two potential donor sites: (i) pyridine ring nitrogen in cyanopyridines or the NH_2 nitrogen in cyanoanilines, and (ii) the nitrile group. Further, the cyano group may be

TABLE I
ANALYTICAL, MAGNETIC MOMENTS AND ELECTRONIC
SPECTRAL DATA

Compound	Colour	Copper % found (Calcd.)	Sulphate % found (Calcd.)	Molar conductance ($\Omega^{-1}\text{cm}^2\text{mole}^{-1}$)	μ_{eff} (B.M.)	Electronic spectral bands and assign- ments (cm^{-1})	
						${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$	
Cu(2-CP) ₂ SO ₄	Blue	17.3 (17.2)	26.0 (26.1)	Insoluble	1.48	11000	13160
Cu(3-CP) ₂ SO ₄	Light blue	17.3 (17.2)	26.3 (26.1)	03	1.48	11160	13070
Cu(4-CP) ₂ SO ₄	Blue	17.0 (17.2)	26.3 (26.1)	03	0.99	11050	13605
						${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$	
Cu(2-CA) _{0.5} SO ₄	Light green	29.0 (28.9)	44.5 (44.0)	01	2.00	10000	12505
Cu(3-CA) ₂ SO ₄	Green	16.1 (15.9)	24.6 (24.3)	01	2.04	10080	12500
						${}^2\text{A}'_1 \rightarrow {}^2\text{E}''$	
Cu(4-CA) ₂ SO ₄	Green	12.4 (12.3)	19.1 (18.7)	01	2.07	12000	

CP = Cyanopyridine, CA = Cyanoaniline.

TABLE 2
 INFRARED SPECTRAL DATA (cm⁻¹)

Compound	ν_{CN}	$\nu_{\text{C}\equiv\text{C}}$ $\nu_{\text{C}\equiv\text{N}}$	Ring vibrations	Coordinated sulphato modes			
				ν_1	ν_2	ν_3	ν_4
2-CP	2236	1582	990				
		1560	652				
			397				
3-CP	2230	1586	970				
		1558	628				
			391				
4-CP	2243	1597	995				
		1550	665				
			368				
Cu(2-CP) ₂ SO ₄	2230	1660	1040	985	455	1162	650
		1600	670			1100	620
			412			1045	605
Cu(3-CP) ₂ SO ₄	2238	1645	1020	990	475	1182	655
		1605	675			1086	645
			430			1020	595
Cu(4-CP) ₂ SO ₄	2238	1650	1020	995	475	1184	635
		1612	675			1075	615
			410			1020	600
		ν_{asymNH}	ν_{symNH}				
2-CA	2240	3440	3360				
3-CA	2240	3440	3360				
4-CA	2242	3440	3362				
Cu(2-CA) _{0.5} SO ₄	2240	3280	3210	980	470	1140	630
						1050	
Cu(3-CA) ₂ SO ₄	2238	3260	3220	990	420	1165	645
						1102	600
						1012	585
Cu(4-CA) ₂ SO ₄	2240	3270	3230	970	445	1165	650
						1105	605
						1025	585

involved in coordination through either (i) the cyano nitrogen on account of its available electron pair, or (ii) the triple bond or π -electrons. Moreover, the 2-cyano- derivatives may act as (i) monodentate ligands bonding via pyridine ring/ NH_2 nitrogen, or the nitrile nitrogen, (ii) bidentate chelating ligands bonding through both the sites simultaneously to the same metal ion, or (iii) bidentate bridging ligands. It should be possible to distinguish between the likely modes of metal-cyanopyridine/cyano-aniline bonding using infrared spectroscopy by observing the effect that

the coordination has on (i) the C \equiv N stretching vibration of the nitrile group, and (ii) the variations of (a) the pyridine ring vibrations in cyanopyridines, or (b) NH stretching modes in cyanoanilines. Coordination through nitrogen of the nitrile group invariably results in an increase in ν_{CN} by at least 30 cm⁻¹ which is attributed to an increase in the CN stretching force constant which in turn is due to an increase in the strength of CN σ -bond¹⁴⁻¹⁷. A decrease in ν_{CN} has been interpreted as resulting from the involvement of the cyano group through its triple bond¹⁸⁻²⁰.

Rock salt region as well as low frequency infrared spectra of the copper(II) sulphate complexes with 2-, 3- and 4-cyanopyridines studied in the present investigations indicate clearly that the cyanopyridines are coordinated to copper(II) via their pyridine ring nitrogen only. In all the cyanopyridine complexes ν_{CN} of the uncoordinated ligands remains almost unaffected. This strongly suggests that the cyano group of these ligands does not participate in coordination, thereby, indicating that the pyridine ring nitrogen is more basic than the nitrile nitrogen. The frequencies of $\nu_{\text{C}=\text{C}}$ and $\nu_{\text{C}=\text{N}}$ vibrations of the aromatic ring have been previously used to assign the coordination site in metal-cyanopyridine complexes. Coordinated pyridine is usually distinguished²¹⁻²⁴ from the free base by a shift in the strong bands at 1580 cm⁻¹ to *ca* 1600 cm⁻¹ and 601 cm⁻¹ and 403 cm⁻¹ bands to *ca* 625 and 420 cm⁻¹, respectively.

In all the copper(II) sulphate complexes with cyanoanilines the ν_{CN} of the uncoordinated ligands remains essentially unchanged thus suggesting that the cyano group of these cyanoanilines does not participate in coordination. In the uncoordinated cyanoanilines the NH asymmetric and symmetric stretching vibrations occur at 3440 and 3360 cm⁻¹, respectively. In all the copper(II) sulphate complexes these bands occur at *ca* 150 cm⁻¹ lower than the corresponding ones in the uncoordinated cyanoanilines. This shifting of the NH stretching bands to lower energies may be attributed^{4, 5, 25, 26} to the weakening of the NH bonds resulting from the drainage of electron density from the nitrogen atom on account of its coordination to copper(II). It is thus clear that the cyanoanilines are present exclusively as terminal NH₂ bonded monodentate ligands in all the copper(II) sulphate complexes and that the NH₂ nitrogen is more basic than the nitrile nitrogen.

It may be pointed out that the introduction of a cyano group, an electron withdrawing group, at 2-, 3- and 4- positions in the pyridine ring (cyanopyridines) or at 2-, 3- and 4- positions in the benzene ring (cyanoanilines) lowers the electron density of the donor nitrogen atom with a substantial decrease in their pK_a values^{27, 28} (Table 3). In particular, the effect of substitution at 2- position upon the base strength is anomalous as compared with 3- and 4- positions. This may be a reflection of such factors as effective charge on the donor nitrogen atom, change in

TABLE 3
 pK_a VALUES OF PYRIDINE, ANILINE AND THEIR CYANO
 DERIVATIVES^{27, 28}

Compound	pK _a	Compound	pK _a
Pyridine	5.23	Aniline	4.62
2-Cyanopyridine	-0.26	2-Cyanoaniline	0.95
3-Cyanopyridine	1.36	3-Cyanoaniline	2.81
4-Cyanopyridine	1.90	4-Cyanoaniline	1.75

the HNH bond angle (in the case of cyanoanilines) and of course the mechanical anharmonicity on 2-position. Hence the metal-ligand bonds in cyanopyridine complexes are expected to be much weaker compared with the corresponding unsubstituted ligands. From a consideration of the pK_a values (Table 3) one can predict the relative magnitude of metal-ligand bond strength as:

Pyridine > 4-cyanopyridine > 3-cyanopyridine ≧ 2-cyanopyridine;

Aniline > 3-cyanoaniline > 4-cyanoaniline ≧ 2-cyanoaniline.

With respect to metal-ligand π -bonding contribution, the decreased electron density on the ring nitrogen in pyridine caused by cyano substitution at different positions is expected to favour the back-donation of π -electron density from the metal.

The observed room temperature magnetic moment values of the copper(II) sulphate complexes with cyanopyridines are sub-normal and are in the range 0.99–1.40 B.M. This may be attributed to some sort of association occurring either through the metal-metal bonding or by magnetic interaction operating through the orbitals of bridging atoms²⁹. On the other hand, the μ_{eff} values of the cyanoaniline complexes (2.00–2.07 B.M.) lie within the range normally expected for copper(II) complexes with an orbitally non-degenerate ground state³⁰. The slight increase from the spin-only value (1.73 B.M.) may be probably because of strong Jahn-Teller distortion operative in copper(II) complexes.

The d⁹ configuration of copper(II) with a ²D free ion term is split in a regular octahedral field into a lower doublet E_g level and an upper triplet T_{2g} level and hence only one spin-allowed transition should result. However, crystal field theory predicts a much larger distortion from cubic symmetry for octahedral copper(II) complexes. Hence the ground state, being Jahn-Teller unstable, shows further splitting of the E_g and T_{2g} levels into B_{1g}, A_{1g} and B_{2g}, E_g levels, respectively, so that even in a complex with six identical donors a regular octahedral configuration is not achieved and the six-coordinate copper(II) complexes have either D_{4h} or C_{4v} symmetry.

Electronic spectra of the blue copper(II) sulphate complexes with cyanopyridines show a strong absorption band at *ca* 13000 cm⁻¹ with a shoulder at *ca* 11000 cm⁻¹ consistent with distorted square planar configuration about the copper(II) ions^{31,32}. Assuming D_{4h} symmetry for the cyanopyridine complexes, the main band and the shoulder may be assigned to the ²B_{1g} → ²E_g and ²B_{1g} → ²A_{1g} transitions, respectively. Because of its low intensity the transition ²B_{1g} → ²B_{2g} is not observed as a separate band in a distorted planar configuration³³.

The electronic spectra of copper(II) sulphate complexes with 2- and 3-cyanoanilines exhibit a very broad band at *ca* 12500 cm⁻¹ suggesting a distorted octahedral stereochemistry³⁴ around copper(II). Though three transitions are expected for copper(II) complexes having such distorted octahedral configurations,³⁵ these transitions are very close in energy and often appear in the form of a broad band envelope.³⁶ The high energy broad band at *ca* 12500 cm⁻¹ observed in the copper(II) sulphate complexes with 2- and 3- cyanoanilines is assigned to the super-imposed transitions ²B_{1g} → ²B_{2g} and ²B_{1g} → ²E_g while the other absorption occurring as a weak shoulder (*ca* 10000 cm⁻¹) on the lower energy side (Table 1) is assigned to the transition ²B_{1g} → ²A_{1g} in distorted octahedral stereochemistry of copper(II) with an approximately C_{4v} symmetry. Electronic spectrum of the 1 : 3 copper(II) sulphate complex with 4-cyanoaniline complex exhibits a single broad band at 12000 cm⁻¹. The position of this band is characteristic of 5-coordinated trigonal bipyramidal geometry around copper(II) rather than square pyramidal. It may be pointed out that square pyramidal³⁷⁻⁴¹ geometry around copper(II) is characterized by a broad band and a shoulder in the 17000-15000 cm⁻¹ and *ca* 12000 cm⁻¹ regions, respectively⁴²⁻⁴⁴. Assuming D_{3h} symmetry for the complex the band at 12000 cm⁻¹ observed in the present complex may be assigned as ²A_{1'} → ²E" transition consistent with trigonal bipyramidal geometry around copper(II).

The free sulphate ion has a highly symmetrical structure. It is tetrahedral, having T_d symmetry and as such has nine vibrational degrees of freedom giving rise to four fundamental vibrations, all of which are Raman active, but only two, both triply degenerate, ν₃ the asymmetric stretching vibration and ν₄ the asymmetric bending vibration, are infrared active. ν₁ the symmetric stretching vibration is theoretically infrared inactive but is generally observed as a weak absorption at *ca* 980 cm⁻¹. It becomes very weakly allowed in the infrared spectra of ionic solid sulphates owing to site symmetry effects but is absent in the spectra of sulphates in aqueous solutions. Upon coordination, the symmetry of the sulphate group is lowered; ν₁ and ν₂ modes become infrared active and splitting of bands due to ν₃ and ν₄ takes place. The observed bands for the free, unidentate and bidentate bridging sulphato groups have been discussed and correlated with changes in the symmetry of the sulphate group.⁴⁵

However, it has been shown that perturbations in the crystal may produce reduced symmetry even when no deviations from the tetrahedral structure of the sulphate group can be detected. The highest frequency band in complexes containing a bidentate bridging sulphato group has been assigned by Nakamoto *et al*⁴⁶ at *ca* 1170 cm^{-1} . A similar band at *ca* 1220 cm^{-1} has been observed by Barraclough and Tobe⁴⁷ in the sulphato-bisethylenediaminecobalt(II) salts in which the sulphate group is considered to be bidentate chelating. The band at *ca* 1220 cm^{-1} has been considered as an evidence for a bidentate chelating sulphato group.

Infrared spectrum of the copper(II) sulphate complex with 2-cyanoaniline shows a strong broad absorption band at 1140–1050 cm^{-1} (masking the ligand bands in this region) and a medium intensity band at 630 cm^{-1} . Since such bands are not observed in the uncoordinated 2-cyanoaniline they are, therefore, identified as ν_3 and ν_4 modes, respectively, due to coordinated sulphato groups characteristic of T_d symmetry. Moreover, a medium intensity band is also observed at 1000 cm^{-1} due to ν_1 vibration of the sulphate group. Although infrared forbidden in the sulphate spectrum with T_d symmetry ν_1 has been reported as a weak band at *ca* 980 cm^{-1} in the spectra of ionic solid sulphates owing to site symmetry effects but is absent in the spectra of sulphates in aqueous solutions. Besides ν_1 , ν_3 and ν_4 of the sulphate groups with T_d symmetry the ν_2 appears as a medium intensity band at 470 cm^{-1} in the low frequency infrared spectrum of this complex. From a consideration of the frequencies due to coordinated sulphate groups (Table 2) it appears that a regular coordination by all the oxygens of the sulphate group occurs and that the sulphate groups retain an essentially T_d symmetry⁴⁸. This fact combined with the terminal $-\text{NH}_2$ bonded 2-cyanoaniline, the electronic spectral bands and the magnetic moment value it is suggested that the complex possesses a highly polymeric structure with an octahedral environment around copper(II) in the solid state.

Infrared spectra of the 1 : 2 copper(II) sulphate complexes with 2-, 3- and 4-cyanopyridines clearly indicate the presence of coordinated sulphato groups. These complexes exhibit bands at *ca* 980 cm^{-1} (ν_1), *ca* 480 cm^{-1} (ν_2), *ca* 1160, 1080, 1020 cm^{-1} (ν_3) and *ca* 650, 620, 600 cm^{-1} (ν_4) consistent with bidentate bridging sulphato groups^{45, 46}. From a consideration of their room temperature magnetic moment values and electronic spectral bands these complexes are assigned binuclear structures with bidentate bridging sulphato groups and terminally pyridine ring nitrogen bonded cyanopyridine molecules involving square planar $[\text{Cu}(\text{L}_2)\text{O}_2]$ moieties in the structure and an overall symmetry lower than D_{4h} (structure 1).

In addition to the ligand bands infrared spectra of the 1 : 2 and 1 : 3 copper(II) sulphate complexes with 3- and 4- cyanoanilines, respectively, exhibit bands at *ca* 990 cm^{-1} (ν_1), *ca* 420 cm^{-1} (ν_2), *ca* 1165, 1105, 1020

cm⁻¹ (ν_3) and *ca* 650, 600, 585 cm⁻¹ (ν_4) consistent with the presence of bidentate bridging sulphato groups^{45,46}. From a consideration of the room temperature magnetic moment values, electronic spectral bands and the bidentate bridging nature of the sulphato groups (i) the 1:2 copper(II) sulphate complex with 3-cyanoaniline is assigned a polymeric, six-coordinated structure with octahedral environments of two terminally aniline NH₂ nitrogen bonded cyanoaniline molecules and two oxygen atoms of the bidentate bridging sulphato groups, and (ii) the 1:3 copper(II) sulphate complex with 4-cyanoaniline is assigned a dimeric, five-coordinated structure with trigonal bipyramidal environment of two oxygen atoms from sulphato groups and three terminally bonded (NH₂) nitrogen atoms of the 4-cyanoaniline molecules around each copper(II) in the solid state (structure 2).

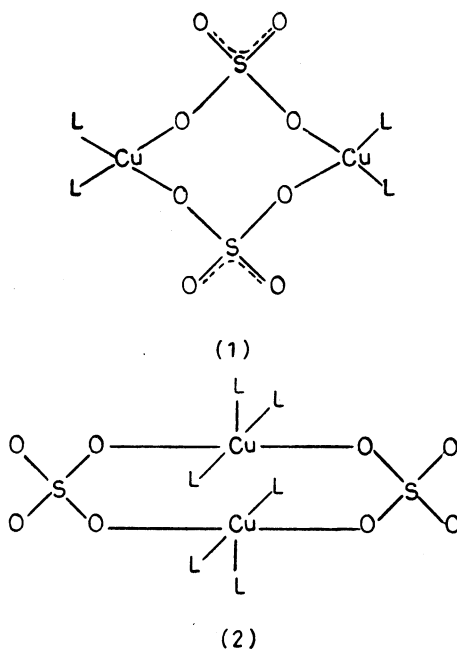


Fig. 1 Structure of Cu(L₂)SO₄ (L=2-CP, 3-CP and 4-CP)

Fig. 2 Structure of Cu(4-CA)₃SO₄

REFERENCES

1. Destrum, *Bull. Soc. Chim.*, **2**, 482 (1876).
2. Saglier, *Compt. rend.*, C VI, 1422.
3. J. V. Dubsy and A. Rabas, *Coll. Czech. Chem. Comm.*, **1**, 528 (1929).
4. I. S. Ahuja, D. H. Brown, R. H. Nuttall and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **27**, 1105, 1625 (1965).

5. I. S. Ahuja, D. H. Brown, R. H. Nuttall and D. W. A. Sharp, *J. Chem. Soc.*, A 938 (1966).
6. V. Scott and E. Joseph, *Chem. Abstr.*, **92**, 42216, 82428 (1980).
7. J. J. Baldwin, E. L. Englehardt, R. Hirschmann, G. S. Ponticello, J. G. Atkinson, B. K. Wasson, C. S. Sweet and A. Seriabine, *J. Med. Chem.*, **23**, 65 (1980).
8. D. E. McClure, J. J. Baldwin, W. C. Randall, T. F. Lyon, K. Mensler, G. F. Lundell, A. W. Raab, D. Cross and E. A. Risley, *J. Med. Chem.*, **26**, 649 (1983).
9. H. Takahata, T. Nakajima and T. Yamazaki, *Chem. Pharm. Bull.*, **32**, 1658 (1984).
10. S. L. Chaev, S. Kirkiacharian, F. Pieri and A. Y. Bou, *Ann. Pharm. Fr.*, **42**, 367 (1984).
11. C. Z. Thompson, L. E. Hill, J. K. Epp and G. S. Probst, *Chem. Absrt.*, **100**, 81039 (1984).
12. K. Yamataka, Y. Matsuoka and A. Shimizu, *Chem. Abstr.*, **107**, 6947 (1987).
13. W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
14. R. A. Walton, *Quar. Rev.*, **19**, 126 (1963).
15. B. N. Storhoff and H. C. Lewis, Jr., *Coord. Chem. Rev.*, **23**, 1 (1977).
16. D. M. Byler and D. F. Shriver, *Inorg. Chem.*, **12** 1412 (1973); **13**, 2697 (1974).
17. B. Swanson and D. F. Shriver, *Inorg. Chem.*, **9**, 1406 (1970).
18. A. Misoro, Y. Uchida and T. Kusa, *Chem. Comm.*, 208 (1969).
19. D. M. Blake and M. Kuboto, *J. Am. Chem. Soc.*, **92**, 2578 (1970).
20. G. A. Tolman, *Inorg. Chem.*, **10**, 1540 (1971).
21. N. S. Gill, R. H. Nuttall D. W. Scaife and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).
22. M. Goldstein, E. F. Mooney, A. Anderson and H. A. Gebbie, *Spectrochim. Acta*, **21**, 105 (1965).
23. C. Postmus, J. R. Ferraro and W. Wozniak, *Inorg. Chem.*, **6**, 2030 (1967).
24. I. S. Ahuja and Raghuvir Singh, *J. Inorg. Nucl. Chem.*, **36**, 1505 (1974).
25. M. A. Jungbauer and C. Curran, *Spectrochim. Acta*, **21**, 641 (1965).
26. I. S. Ahuja, C. L. Yadava and S. Tripathi, *Synth. React. Inorg. Met.-Org. Chem.* **18**, 433 (1988).
27. J. M. Vandenberg, C. Henrich and S. G. V. Berg, *Anal. Chem.*, **26**, 726 (1954).
28. S. F. Mason, *J. Chem. Soc.*, 1247 (1959).
29. B. N. Figgis "Introduction to Ligand Fields" Wiley Eastern Limited, New Delhi, 1966.
30. B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, **6**, 37 (1964).
31. I. S. Ahuja, Raghuvir Singh and C. P. Rai, *Trans. Met. Chem.*, **2**, 257 (1977).
32. M. H. Senar and A. S. R. Murthy, *J. Inorg. Nucl. Chem.*, **42**, 815 (1980).
33. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968.
34. B. J. Hathaway and A. A. A. Tomlinson, *Coord. Chem. Rev.*, **5**, 1 (1970).

35. C. A. Agamber and K. G. Orrell, *J. Chem. Soc.*, A, 897 (1969).
36. D. W. Smith, *Inorg. Chem.*, **5**, 2236 (1966).
37. H. Elliot, B. J. Hathaway and R. C. Slade, *J. Chem. Soc.*, A, 1443 (1966).
38. R. C. Slade, A. A. G. Tomlinson, B. J. Hathaway and D. E. Billing, *J. Chem. Soc.*, A, 61 (1968).
39. B. J. Hathaway, I. M. Proctor, R. C. Slade and A. A. G. Tomlinson, *J. Chem. Soc.*, A, 2219 (1969).
40. A. Jaggi, S. Chandra and K. K. Sharma, *Polyhedron*, **4**, 163 (1985).
41. J. Gracia, M. Molla and J. Borrás, *Polyhedron*, **4**, 757 (1985).
42. J. N. Brown, H. R. Eichelberger, E. Schaeffer, M. L. Good and L. M. Trefonas, *J. Am. Chem. Soc.*, **93**, 6290 (1971).
43. J. N. Brown and L. M. Trefonas, *Inorg. Chem.*, **12**, 1730 (1973).
44. T. M. Suzuki, S-ichi Kamiyana and T. Kimura, *Bull. Chem. Soc.*, Japan, **51**, 1094 (1978).
45. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds" 4th Edition, John Wiley, New York, 1986.
46. K. Nakamoto, J. Fujita, S. Tanaka and M. Kobayashi, *J. Am. Chem. Soc.*, **79**, 4904 (1957).
47. C. G. Barraclough and M. L. Tobe, *J. Chem. Soc.*, 1993 (1961).
48. I. S. Ahuja, *Indian J. Chem.*, **9**, 173 (1971).

[Received: 4 September 1989; Accepted: 8 October 1989]

AJC-101